Electrophosphorescence and Delayed Electroluminescence from Pristine Polyfluorene Thin-Film Devices at Low Temperature

S. Sinha,[1] C. Rothe,[1] R. Güntner,[2] U. Scherf,[2] and A. P. Monkman[1,*]

[1]*Organic Electroactive Materials Research Group, Department of Physics, University of Durham, South Road, Durham DH1 3LE, England*

[2]*Institut für Physikalische Chemie und Theoretische Chemie Polymerchemie, Universität Potsdam, Karl-Liebknecht-Strasse 24-25, Haus 25, 14476 Golm, Germany*

(Received 28 October 2002; published 25 March 2003)

Intrinsic long-lived electrophosphorescence and delayed electroluminescence from a conjugated polymer (polyfluorene) thin film is observed for the first time at low temperature. From bias offset voltage dependent measurements, it is concluded that the delayed fluorescence is generated via triplet-triplet annihilation. A fast and efficient triplet exciton quenching by charge carriers is found to occur in the active polymer layer of the working devices.

DOI: 10.1103/PhysRevLett.90.127402 PACS numbers: 78.55.Kz, 78.60.Fi

Since the first report of electroluminescence (EL) in polymer light emitting diodes (PLEDs) by Burroughes *et al.* [1], a great deal of research has been devoted to understanding the photophysical properties of conjugated polymers. Luminescence in PLEDs is usually governed by the radiative recombination of singlet excitons. It follows from spin statistics and spin dependent recombination that between 50% to 75% of all recombination events within a PLED can produce triplet excitons, thus as little as 25% generates singlet excitons [2,3]. For poly(9,9-bis(2-ethylhexyl)fluorene-2,7-diyl) (PF2/6), it is suggested that less than one triplet exciton is formed for every singlet exciton [3]. Even given the latter scenario, efficient radiative triplet recombination would enhance PLED performance by at least 50%. Therefore, characterizing the nature and photophysics of triplet states of light emitting polymer systems is extremely important. Direct spectroscopic information on triplet states of conjugated polymers can be obtained from delayed emission lasting up to several seconds, i.e., phosphorescence (Ph) and delayed fluorescence (DF). However, DF in conjugated polymers can originate from either triplet-triplet annihilation (TTA) [4] or recombination of geminate (Coulombically bound) electron-hole pairs effectively trapped within the active polymer layer [5].

It is already reported that conjugated polymers emit Ph and DF at low temperature upon photoexcitation [5–7]. However, until now, there is no report of *intrinsic* electrophosphorescence from conjugated polymers commonly used for PLED fabrication. There have been several reports in the literature on the observation of ''after glow'' from PLEDs operated in pulsed mode [8–10]. However, this has invariably been ascribed to both fast (15 ns) and slow (1 μs) decaying components of the swept out charge carriers upon switch off [9]. No spectroscopy was made on this after glow light to determine its true origin. Several workers observed electrophosphorescence from PLEDs by doping the polymer layer with phosphorescent dye molecules containing heavy metal atoms (platinum) [11,12]. Very recently, Lupton *et al.* [13] reported electrophosphorescence from a diaryl (diphenyl)-substituted derivative of ladder-type poly(paraphenylene) (PhLPPP) by incorporating covalently bound heavy metal atoms (palladium) into the polymer backbone, thereby increasing the spin-orbit coupling and, hence, the triplet population. In this Letter, we report for the first time the observation of truly *intrinsic* electrophosphorescence and delayed electroluminescence from pristine PF2/6 thin film. This is a very important observation keeping in mind that the real photophysics in the active polymer layer in PLEDs is governed by charge recombination and not photoexcitation. Here, we note that, although polyfluorenes have been under intensive study for many years, its electrophosphorescence could not be observed before mainly because of the lack of experimental sensitivity. The complete experimental setup (*vide infra*), presently available in our laboratory, makes it possible to detect and time gate the weak electrophosphorescence signal from polyfluorene based devices, which requires a N_2 glove box to fabricate the PLEDs, a fast pulse generator to apply the driving bias voltage pulses across the devices, and a high gain charge-coupled device (CCD) camera to record the electrophosphorescence signal.

PF2/6 is widely used as the active layer in bright EL devices [14,15]. The general spectroscopic features of PF2/6 have been reported in several publications [16,17]. From photoluminescence (PL) measurements, it is already known that PF2/6 thin film emits Ph and DF at low temperature (<100 K) upon photoexcitation [6,7]. Based on the PL intensity dependence of Ph and DF on the excitation pulse energy and decay kinetics measurements, it was argued that DF in PF2/6 thin film originates from TTA [6,7]. It is to be noted that prompt fluorescence of PF2/6 exhibits a weak keto defect emission band at about 515 nm upon photoexcitation [18]. However, the keto defect emission band becomes very

prominent when the polymer film is excited via charge recombination due to charge carrier trapping. In order to avoid this unwanted keto defect emission band, we used PF2/6 endcapped with bis(4-methylphenyl)phenylamine with a monomer/endcapper feed ratio (mol/mol) as 96:4 (PF2/6am4) (inset of Fig. 1) in the present work. The keto defect emission band is almost completely suppressed in the prompt fluorescence from the devices based on PF2/6am4 as the active emitting layer [18].

LEDs were fabricated on solution etched indium tin oxide (ITO) coated glass substrates as described previously [15]. Briefly, a 30 nm thick hole-transporting layer (HTL) of poly(3,4-ethylenedioxythiophene) doped with polystyrene sulphonated acid (PEDOT) was spin coated on the ITO layers and dried overnight. PF2/6am4 was dissolved in toluene and the solution was spin coated onto the HTL coated substrates to give an active layer with a thickness of 80 nm. The synthesis of the conjugated polymer PF2/6am4 has been described elsewhere [18,19]. Calcium cathodes (50 nm) were evaporated onto the polymer layer, followed by a capping layer of aluminum (50 nm), in a N_2 glove box. A Hewlett-Packard pulse generator (8114A) was used to apply the bias voltage pulses with a typical rise and fall time of 10 ns. For bias offset dependent measurements, a unity voltage gain differential amplifier was used with a Keithley 2400 used to provide dc bias offset voltages. The electroluminescence emitted by the device was dispersed by a monochromator (TRIAX 180, JOBIN YVON-SPEX) and recorded by a red enhanced, gated intensified CCD camera (4 Picos, Stanford Computer Optics) [7]. This camera permits variable integration and delay times allowing time-resolved detection of electroluminescence with very high gain from 200 ps up to 80 s after the device is turned off. All experiments were performed under a dynamical vacuum of $<10^{-4}$ Torr in a temperature controlled helium cryostat.

The prompt fluorescence spectra of PF2/6am4 thin film under the application of a bias voltage at low temperature (28 K) (Fig. 1) are identical to those reported by several authors as observed upon photoexcitation [6,7]. The solid line in Fig. 1 shows the delayed electroluminescence of PF2/6am4 thin film at 28 K. The device is kept ON for 5 ms (electric pulse width), and then a delay time of 5 ms is applied after which the delayed emission is measured with an integration time (detection gate width) of 70 ms. In this way, the weak delayed emission can be observed without being swamped by the intense prompt fluorescence. The delayed emission spectra exhibit similar features to those previously observed by several workers by PL measurements [6,7]. The high energy part of the delayed emission spectra is identical to the prompt fluorescence spectra at 28 K and is attributed to DF. The low energy part of the delayed emission spectra exhibits two vibronic bands, the first one at 2.19 eV and the second one at 2.02 eV. It possesses a vibronic structure similar to that of the prompt fluorescence spectra at 28 K and is logically attributed to Ph. It is noteworthy that this is the first observation of *intrinsic* electrophosphorescence in a conjugated polymer. The importance of this observation lies in the fact that it gives a straightforward way to study the triplet state photophysics in the active polymer layer of PLEDs.

In order to see the origin of the DF observed in the present investigations, we measured the delayed emission spectra at 28 K at a drive bias voltage of 12 V, as a function of bias offset voltage after the device is turned off. The bias offset of the voltage pulse was varied below the turn-on voltage of the device (4.0 V) [20], keeping the pulse amplitude constant at 12 V. As shown in Fig. 2,

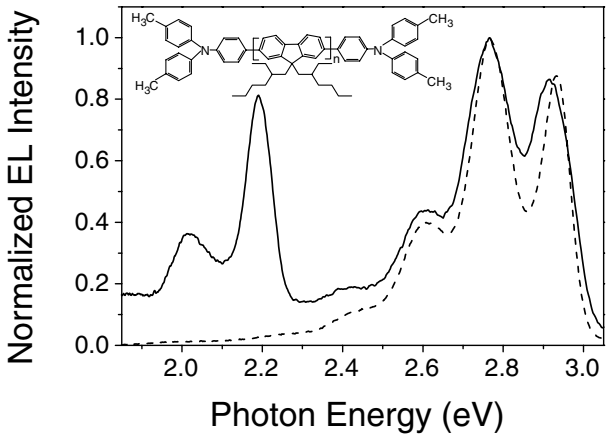

FIG. 1. Prompt fluorescence spectra (dashed line: bias = 11 V) and delayed emission spectra (solid line: bias = 11 V, pulse width = 5 ms, delay = 5 ms, gate width = 70 ms) of PF2/6am4 thin film device at 28 K. The inset shows the chemical structure of PF2/6am4.

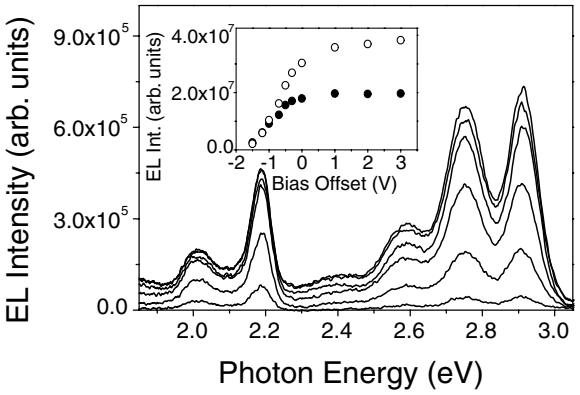

FIG. 2. Delayed emission spectra of PF2/6am4 thin film device at 28 K (bias = 12 V, pulse width = 5 ms, delay = 5 ms, gate width = 70 ms) with different bias offset voltages (from top to bottom: +3.0 V, +1.0 V, 0 V, −0.5 V, −1.0 V, −1.5 V). The inset shows the bias offset dependence of the integral EL intensities of the delayed emission bands (●: Ph; ○: DF).

forward bias offset has little effect on the EL intensities of either Ph or DF. However, the EL intensities of Ph as well as DF decrease gradually with the increase in reverse bias offset voltage (inset of Fig. 2). If geminate pair recombination is responsible for the observed DF, then increase in reverse bias offset voltage should lower the DF intensity without affecting the Ph intensity at all [13]. Thus, our findings clearly rule out geminate pair recombination to be responsible for the observed DF. The fact that both Ph and DF intensities decrease (the latter albeit faster than the former) with the increase in reverse bias offset voltage strongly suggests that both have the same origin, i.e., triplets. Thus, the DF observed upon charge recombination must originate from TTA. This is further supported by the fact that, as the bias voltage is increased from 7 to 12 V (keeping the bias offset voltage constant at 0 V), the EL intensities of Ph and DF obey a $I_{\mathrm{DF}} \alpha I_{\mathrm{Ph}}^{1.4}$ dependency over the entire bias voltage range (figure not shown). This superlinear dependence of DF intensity on Ph intensity strongly indicates that TTA is responsible for the observed DF. Earlier, from PL measurements, several authors reported similar dependence of DF intensity on Ph intensity based on the excitation energy dependence and suggested TTA to be responsible for the DF observed upon photoexcitation [6,7].

The decrease in Ph intensity with an increase in reverse bias offset voltage (Fig. 2) seems to be due to the quenching of triplet population by charge carriers. It is well known that under the application of a bias voltage a fraction of the injected charge carriers is trapped near the interface regions of the polymer layer and the electrodes leading to accumulation of space charge and thus to local changes of the internal electric field [8–10,21–23]. Pinner *et al.* [8] reported that the trapped charge carriers give rise to a sharp discharging current spike (of the order of μs) after the device is turned off. In fact, we observed a weak short-lived DF (of the order of μs) in polyfluorene based devices, which can be detected at 28 K as well as at 292 K (no electrophosphorescence can be detected at 292 K). The short-lived DF grows in intensity as the temperature is increased from 28 to 292 K and is attributed to the space charge effect, the details of which will be discussed in a separate communication. However, it is noteworthy that the short-lived DF signal is found to be quenched significantly under the application of a reverse bias offset voltage. This indicates that a part of the trapped charge carriers is swept out to the respective electrodes in the presence of a reverse bias offset voltage after the device is switched off. While moving to the respective electrodes, some of these charge carriers quench the triplet population, thereby quenching Ph intensity and subsequently DF intensity, to some extent depending on the magnitude of the reverse bias offset voltage. This kind of triplet exciton quenching by charge carriers has been extensively studied in molecular crystals [24] and is expected to play a significant role on the triplet population in PLEDs. However, little information is available about this process in conjugated polymers because of the lack of experimental data. Our observations indicate that triplet exciton quenching by charge carriers is indeed an important process in devices based on conjugated polymers and, hence, must be taken into account while determining the ratio of singlet to triplet population in working PLEDs accurately.

At delay times <30 ms, the DF intensity decays in a power law fashion, $I_{\mathrm{DF}} \alpha t^{m}$ (inset of Fig. 3). In integrated kinetics, the value of m is found to be -0.2 at delay times <3 ms and approaches a value of -0.5 for delay times exceeding 3 ms. So, in real kinetics the value of m varies from -1.2 to -1.5 in the respective time domains. Hertel *et al.* [6] observed similar behavior for the decay kinetics of DF in the same delay time region upon photoexcitation, although the values of m observed in the present work are somewhat lower than those reported by them. At delay times > 60 ms, the Ph as well as the DF exhibit a monoexponential decay as shown in Fig. 3. This is a true differentiated kinetics as the channel width of the detection (40 ms) is much shorter than the applied delay times. The lifetimes of Ph and DF are found to be 217 and 97 ms, respectively. Thus, the decay time of DF is almost half of that of Ph indicating that the phenomenology regarding Ph and DF is the same. This again confirms that the DF observed upon charge recombination originates from TTA. Our results are basically similar to the decay kinetics of Ph and DF earlier observed by several authors from PL measurements [6,7]. However, these authors reported much longer lifetimes for Ph as well as DF. Finally, the reverse bias offset voltage is found not to affect the decay kinetics of either Ph or DF observed in the ms time domain. Clearly, the quenching of Ph intensity and, subsequently, DF intensity by charge carriers

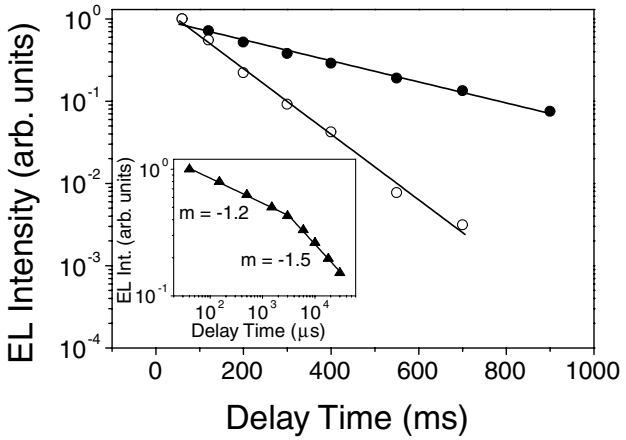

FIG. 3. Decay curves of Ph (●) and DF (○) of PF2/6am4 thin film device at 28 K for delay times > 60 ms (bias = 12 V, pulse width = 1 ms, gate width = 40 ms). The inset shows the decay curve of DF for delay times <30 ms (bias = 12 V, pulse width = 400 μs, gate width = 100 ms).

under the application of a reverse bias offset voltage (*vide supra*) is too fast (probably in the submicrosecond time domain) to affect the decay kinetics of the long-lived delayed emission bands.

In conclusion, we reported the first observation of truly *intrinsic* long-lived (of the order of ms) electrophosphorescence in PLEDs at low temperature using polyfluorene as the active emitting layer. We also observed a delayed fluorescence at long delay times (of the order of ms). From bias offset voltage dependence of the EL intensities of Ph and DF, it is concluded that the DF originates from TTA. Superlinear dependence of the DF intensity on Ph intensity, obtained by increasing the bias voltage, again confirms that TTA is responsible for the observed DF. At delay times <30 ms, the DF decays in a power law fashion with an exponent value of -1.5. Both Ph and DF decay monoexponentially at long delay times (>60 ms) with lifetimes of 217 and 97 ms, respectively, indicating that the DF is generated via TTA. However, the decay kinetics of electrically induced Ph and DF are found to be somewhat different from those observed earlier by PL measurements. A fast (submicrosecond) triplet exciton quenching by charge carriers is found to occur very efficiently in the PLEDs, and this quenching process must be taken into account while determining the ratio of singlet to triplet population in working devices accurately.

The authors wish to thank EPSRC for funding (GR/M86040 and GR/R19687). A. P. M. thanks the Leverhulme Foundation for support.

*Corresponding author.
Electronic address: a.p.monkman@durham.ac.uk

[1] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn, and A. B. Holmes, Nature (London) **347**, 539 (1990).
[2] M. A. Baldo, D. F. O'Brien, M. E. Thompson, and S. R. Forrest, Phys. Rev. B **60**, 14 422 (1999).
[3] M. Wohlgenannt, K. Tandon, S. Mazumdar, S. Ramasesha, and Z. V. Vardeny, Nature (London) **409**, 494 (2001).
[4] M. Pope and C. E. Swenberg, *Electronic Processes in Organic Crystals and Polymers* (Oxford University Press, New York, 1999).
[5] Yu. V. Romanovskii, A. Gerhard, B. Schweitzer, U. Scherf, R. I. Personov, and H. Bässler, Phys. Rev. Lett. **84**, 1027 (2000).
[6] D. Hertel, R. Guentner, U. Scherf, and H. Bässler, J. Chem. Phys. **115**, 10 007 (2001).
[7] C. Rothe, R. Guentner, U. Scherf, and A. P. Monkman, J. Chem. Phys. **115**, 9557 (2001).
[8] D. J. Pinner, R. H. Friend, and N. Tessler, J. Appl. Phys. **86**, 5116 (1999).
[9] D. J. Pinner, R. H. Friend, and N. Tessler, Appl. Phys. Lett. **76**, 1137 (2000).
[10] J. Wang, R. G. Sun, G. Yu, and A. J. Heeger, J. Appl. Phys. **91**, 2417 (2002).
[11] D. F. O'Brien, M. A. Baldo, M. E. Thompson, and S. R. Forrest, Appl. Phys. Lett. **74**, 442 (1999).
[12] V. Cleave, G. Yahioglu, P. LeBarny, R. H. Friend, and N. Tessler, Adv. Mater. **11**, 285 (1999).
[13] J. M. Lupton, A. Pogantsch, T. Piok, E. J. W. List, S. Patil, and U. Scherf, Phys. Rev. Lett. **89**, 167401 (2002).
[14] M. Gross, D. C. Muller, H. G. Nothofer, U. Scherf, D. Neher, C. Brauchle, and K. Meerholz, Nature (London) **405**, 661 (2000).
[15] R. W. T. Higgins, A. P. Monkman, H.-G. Nothofer, and U. Scherf, Appl. Phys. Lett. **79**, 857 (2001).
[16] M. Ariu, D. G. Lidzey, and D. D. C. Bradley, Synth. Met. **111**, 607 (2000).
[17] A. J. Cadby, P. A. Lane, H. Mellor, S. J. Martin, M. Grell, C. Giebeler, and D. D. C. Bradley, Phys. Rev. B **62**, 15 604 (2000).
[18] T. Miteva, A. Meisel, W. Knoll, H. G. Nothofer, U. Scherf, D. C. Müller, K. Meerholz, A. Yasuda, and D. Neher, Adv. Mater. **13**, 565 (2001).
[19] U. Scherf and E. J. W. List, Adv. Mater. **14**, 477 (2002).
[20] R. W. T. Higgins, H.-G. Nothofer, U. Scherf, and A. P. Monkman, J. Appl. Phys. **91**, 99 (2002).
[21] F. Feller, D. Geschke, and A. P. Monkman, Appl. Phys. Lett. **79**, 779 (2001).
[22] Y. Z. Wang, D. D. Gebler, L. B. Lin, J. W. Blatchford, S. W. Jessen, H. L. Wang, and A. J. Epstein, Appl. Phys. Lett. **68**, 894 (1996).
[23] R. Österbacka, A. J. Pal, K.-M. Källman, and H. Stubb, J. Appl. Phys. **83**, 1748 (1998).
[24] M. Pope and C. E. Swenberg, *Electronic Processes in Organic Crystals and Polymers* (Oxford University Press, Oxford, 1999).